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Stability of AL-Sn melts at 973 K by molecular interaction volume model

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Abstract
The excess stability function of Al-Sn melts at 973 K is discussed in terms of concentration fluctuations which is determined from the second derivative of Gibbs free energy of mixing. The molecular interaction volume model has been adopted to explain the excess free energy of mixing, free energy of mixing, concentration fluctuations and excess stability function for Al-Sn melts at 973 K. The theoretical data for excess free energy of mixing, free energy of mixing and concentration fluctuations are in well harmony with the correlated experimental data. The experimentally observed asymmetries in excess free energy of mixing as well as free energy of mixing are successfully explained. The theoretical findings confirm the segregating character of Al-Sn melts at 973 K.

Keywords: Excess stability function; concentration fluctuations; free energy of mixing; MIVM model; excess free energy of mixing

Introduction

The Al-Sn and Al-Sn based alloys like Al-Sn-Zn, Al-Cu-Zn, Al-Ga-Zn etc have ample applications in electronics as solders, in industries such as aerospace, marine and automotive industries etc as bearing materials due to their improved physical, structural, mechanical, transport properties etc [1, 2, 3]. The phase diagram [4] of Al-Sn melts at 973 K represents the positive values of Gibbs free energy of mixing, G_M^E and enthalpy of mixing, H_M relative to the composition of Al i.e. x_{Al} = 0.1 to 0.9. This indicates the segregation in Al-Sn melts at 973 K [5]. The composition dependence of the activity of Al and Sn shows the positive deviations from ideal mixing behavior which indicates the segregation in Al-Sn melts. Again, the G_M^E, free energy of mixing, and G_M exhibit the asymmetries relative to the concentration about x = 0.5. The structural and thermophysical properties of Al-Sn melts have attracted several investigators [6, 7, 8, 9]. However, the data related to an interesting property like excess stability function, E^{XS} [10] of Al-Sn melts are not available in the literature. Therefore, in present work, the E^{XS} for Al-Sn melts has been discussed in terms of the concentration fluctuations, $S_{CC}(0)$. The present theoretical exploration of G_M^E, G_M, $S_{CC}(0)$ and E^{XS} of Al-Sn melts at 973 K is based on a statistical mechanical approach known as MIVM i.e. molecular interaction volume model [11, 12]. The MIVM model is found to be suitable to explain the thermodynamic behavior of several alloys like Zn-Bi, Au-Sn-Bi, Au-Sn-Zn, Ag-Au-Cu etc [13, 14, 15, 16, 17].

Formalism

The MIVM model [11, 12] is utilized to study the concentration dependence of G_M^E, G_M, $S_{CC}(0)$ and E^{XS} of Al-Sn melts at 973 K. The analytical expressions have deduced for G_M^E, G_M, $S_{CC}(0)$ and E^{XS} of a binary liquid alloy in the light of MIVM model

2.1 $S_{CC}(0)$ and E^{XS} of a binary liquid alloy

The excess stability function, E^{XS} initiated by Darken [10] may be expressed as

$$\frac{E^{XS}}{RT} = Scc(0))^{-1} - (S_{cc}^{id}(0))^{-1} \tag{1}$$

Obviously, E^{XS} = positive for ordering alloy, E^{XS} = negative for segregating alloy and E^{XS} = 0 for ideal alloy depending upon the conditions that $S_{cc}(0)<S_{cc}^{id}(0)$, $S_{cc}(0)>S_{cc}^{id}(0)$, and $S_{cc}(0)=S_{cc}^{id}(0)$ respectively.
The $S_{cc}(0)$ is related to G_M as [5, 18]

$$S_{cc}(0) = RT\left(\frac{\partial^2 G_M}{\partial x_i^2}\right)_{T,P,N}^{-1} = RT\left(\frac{\partial^2 G_M}{\partial x_j^2}\right)_{T,P,N}^{-1} \tag{2}$$

Where, $G_M = G_M^E + G_M^{id}$ (3)

$$\Rightarrow G_M = G_M^E + RT\left[x_i \ln x_i + x_j \ln x_j\right] \tag{4}$$

with G_M^E = excess free energy of mixing of the binary alloy

x_i and x_j = concentrations of the components I and j of the alloy

2.2 G_M^E, G_M, and $S_{cc}(0)$ of a binary liquid alloy

The excess free energy of mixing in light of MIVM model [11] is represented as

$$\frac{G_M^E}{RT} = x_i \ln\left(\frac{V_{mi}}{x_i V_{mi} + x_j V_{mj} A_{ji}}\right) + x_j \ln\left(\frac{V_{mj}}{x_j V_{mj} + x_i V_{mi} A_{ij}}\right) - \frac{x_i x_j}{2}\left(\frac{Z_i A_{ji} \ln A_{ji}}{x_i + x_j A_{ji}} + \frac{Z_j A_{ij} \ln A_{ij}}{x_j + x_i A_{ij}}\right) \tag{5}$$

where, A_{ij} and A_{ji} stands for energy interaction parameters, Z_i and Z_j = coordination numbers of the elements i and j are respectively in first shell. The energy interaction parameters may be defined as [11]

$$A_{ji} = \exp\left[-\frac{\varepsilon_{ji}-\varepsilon_{ii}}{kT}\right] \text{ and } A_{ij} = \exp\left[-\frac{\varepsilon_{ij}-\varepsilon_{jj}}{kT}\right] \tag{6}$$

Where, ε_{ii}, ε_{jj} and ε_{ji} = interaction energies between $i-i$, $j-j$ and $i-j$ pairs respectively, k and T = Boltzmann constant and temperature respectively. It is mention that $\varepsilon_{ij} = \varepsilon_{ji}$.
Using equations (4) and (5) in equation (2), one can obtain

$$Scc(0) = \frac{x_i x_j}{1 + x_i x_j f(x_i x_j)} \tag{7}$$

Where,

$$f(x_i, x_j) = \frac{V_{mj}A_{ji} - V_{mi}}{x_i V_{mi} + x_j V_{mj} A_{ji}} + \frac{V_{mi}A_{ij} - V_{mj}}{x_j V_{mj} + x_i V_{mi} A_{ij}} + \frac{V_{mj}A_{ji}(V_{mj}A_{ji} - V_{mi})}{(x_i V_{mi} + x_j V_{mj} A_{ji})^2}$$
$$+ \frac{V_{mi}A_{ij}(V_{mi}A_{ij} - V_{mj})}{(x_j V_{mj} + x_i V_{mi} A_{ij})^2} + \left[\frac{Z_i A_{ji}^2 \ln A_{ji}}{(x_i + x_j A_{ji})^3} + \frac{Z_j A_{ij}^2 \ln A_{ij}}{(x_j + x_i A_{ij})^3}\right] \tag{8}$$

Since $G_M = G_M^{id}$ for ideal mixing, hence equations (7) and (8) yield

$$S_{cc}^{id}(0) = x_i x_j \tag{9}$$

Again, the experimental data for $S_{cc}(0)$ can be computed on using the experimental data of activity, $a_k (k = i, j)$ of the binary alloy from the relation are [5, 18, 19, 20]

$$S_{cc}(0) = a_i x_j \left(\frac{\partial a_i}{\partial x_i}\right)^{-1} = a_j x_i \left(\frac{\partial a_j}{\partial x_j}\right)^{-1} \tag{10}$$

In infinite dilute solution region such as x_i or $x_j \to 0$, the activity coefficients of the constituents i and j may be represented by

$$\ln \gamma_i^{\infty} = 1 - \ln\left(\frac{V_{mj} A_{ji}}{V_{mi}}\right) - \frac{V_{mi} A_{ji}}{V_{mj}} - \frac{1}{2}\left(Z_i \ln A_{ji} + Z_j A_{ij} \ln A_{ij}\right) \tag{11}$$

And

$$\ln \gamma_j^{\infty} = 1 - \ln\left(\frac{V_{mi} A_{ij}}{V_{mj}}\right) - \frac{V_{mj} A_{ji}}{V_{mi}} - \frac{1}{2}\left(Z_j \ln A_{ij} + Z_i A_{ji} \ln A_{ji}\right) \tag{12}$$

The equation (11) and (12) are solve simultaneously to determine the values of A_{ij} and A_{ji}

3. Results and Discussions

3.1 G_M^E and G_M of Al-Sn binary melts at 973 K

The analytical equations (4) and (5) are employed to assess the G_M and G_M^E of Al-Sn melts at 973 K.. The coordination numbers of Al and Sn are determined from the relation [11]

$$Z_i = \frac{4\sqrt{2\pi}}{3}\left(\frac{r_{mi}^3 - r_{oi}^3}{r_{mi} - r_{oi}}\right)\rho_i r_{mi} \exp\left(\frac{\Delta H_{mi}(T_{mi} - T)}{Z_C R T_{mi}}\right) \tag{13}$$

Where, ΔH_{mi} the enthalpy at T_{mi}, the melting temperature, $\rho_i = N_i V_i = \frac{0.6022}{V_{mi}}$ = the molecular number density, r_{mi} and r_{oi} = initial and first peak values for radial distribution function of pure component in molten state , R = molar gas constant and Z_C = co-ordination number of closed packed structure = 12. The radial distances may be represented by

$$r_{oi} = 0.918 d_{\text{cov},i} \text{ and } r_{mi} = \sigma_i \tag{14}$$

Where, d_{cov} represents atomic covalent diameter and σ_i the atomic diameter.

The needed parameters of pure Al and Sn are presented in Table 1 [21]. The parameters A_{ji} and A_{ij} are evaluated on solving equations (11) and (12) simultaneously by Newton - Rapson method. For this, γ_i^{∞} and γ_j^{∞} i.e. infinite dilute activity coefficients [4] are required which are presented in Table 2. The approximated values of A_{ji} and A_{ij} are slightly altered in order to achieve a good harmony between the theory and experiment [4] for G_M^E of Al-Sn melts at 973 K. The reasonable values of A_{ji} and A_{ij} are also incorporated in Table 2

Table 1: Needed parameters for pure Al and Sn [21]

Metal, i	ΔH_{mi} (KJ/mol)	σ_i (×10^{-8}cm)	r_{oi} (×10^{-8} cm)	V_{mi} (cm^3/mol)
Al	10.46	2.78	2.28	11.3[1+1.5×10^{-4}(T-933)]
Sn	7.07	3.14	2.68	17.0[1+0.87×10^{-4}(T-505)]

Table 2: Estimated values of A_{ij}, A_{ji}, Z_i and Z_j for the constituents of Al-Sn molten alloys at 973 K

$i-j$	T(K)	A_{ij}	A_{ji}	Z_i	Z_j	γ_i^{∞}	γ_j^{∞}
Al-Sn	973	0.6664	1.0411	9.48	9.09	2.706	6.639

The computed values of $\frac{G_M^E}{RT}$ and $\frac{G_M}{RT}$ relative to the composition of Al for Al-Sn melts at 973 K exhibit excellent harmony with the corresponding experimental data [4] as shown in Fig 1. In complete composition region, x_{Al} = 0.1 to 0.9, G_M^E exhibits positive value at each concentration with maximum values at x_{Al} = 0.60 i.e. 0.3570 (Theory) and 0.3570 (Experiment). This indicates the segregating nature of Al-Sn melts at 973 K [5] i.e. there is a tendency of similar atoms association (Al-Al or Sn-Sn) as closest neighbors. Again, $\frac{G_M}{RT}$ illustrates the minimum values at x_{Al} = 0.40 i.e. - 0.3498 (Theory) and -0.3508 (Experiment). Thus, the asymmetries in $\frac{G_M^E}{RT}$ and $\frac{G_M}{RT}$ successfully described by MIVM model.

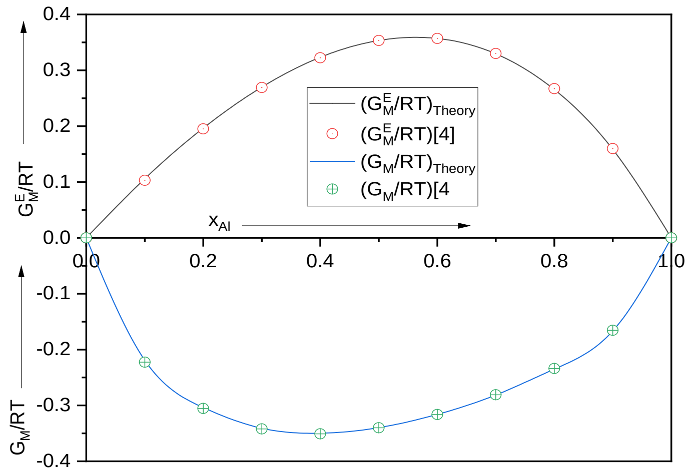

Fig. 1 (G_M^E/RT & G_M/RT) vs x_{Al} for Al-Sn melts at 973 K

3.2 $S_{cc}(0)$ and E^{XS} of Al-Sn melts at 973 K

The $S_{cc}(0)$ computed using equations (7) and (8) for Al-Sn melts at 973 K is exhibited in Fig. 2 relative to the concentration of Al. The values of $S_{cc}^{id}(0)$ are also incorporated in Fig. 2. The positive departure of $S_{cc}(0)$ from $S_{cc}^{id}(0)$, is clearly observed in the complete range of concentration i.e. x_{Al} = 0.1 to 0.9 which is an indication of the segregation in Al-Sn melts at 973 K [5]. For the shake of comparison, the experimental data of $S_{cc}(0)$ [4] are also included in Fig. 2 which shows a well uniformity having maximum values at x_{Al} = 0.60 i.e. = 0.955 (Theory) and 0.942 (Experiment). This corresponds to the asymmetric behavior of Al-Sn melts at 973 K.

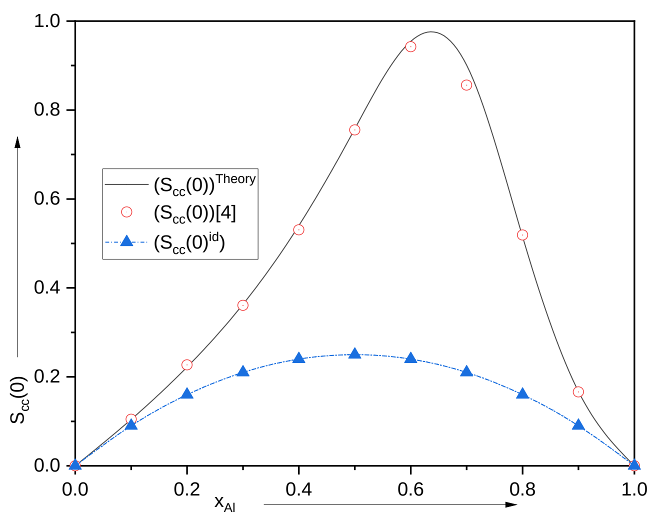

Fig. 2 $S_{cc}(0)$ vs x_{Al} for Al-Sn melts at 973 K

The Fig. 3 shows the variation of E^{XS}/RT relative to the composition of Al for Al-Sn melts at 973 K, computed from equation (1) are illustrated in Fig. 3. Obviously, E^{XS}/RT indicates the negative values in the complete region of composition, x_{Al} = 0.1 to 0.9 for Al-Sn melts at 973 K. This exhibits the segregating nature of Al-Sn melts at 973 K [22, 23].

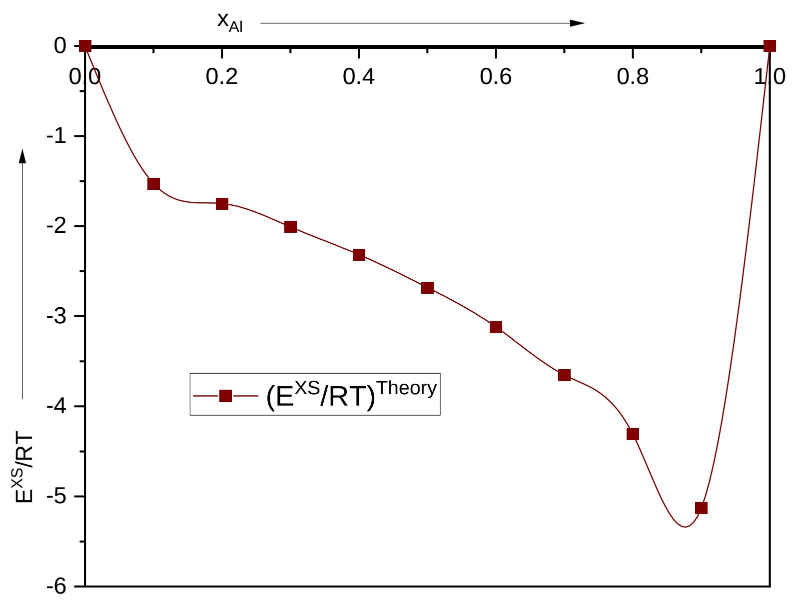

Fig. 3 E^{XS}/RT vs x_{Al} for Al-Sn melts at 973 K

Conclusions

The concentration variations of G_M^E, G_M and $S_{cc}(0)$ for Al-Sn melts at 973 K indicate the asymmetric character of Al-Sn melts at 973 K around x_{Al} = 0.5. The theoretical data of of G_M^E, G_M and $S_{cc}(0)$ exhibit well harmony with the corresponding experimental findings available in the literature. The theoretical prediction of E^{XS}/RT confirms the segregating behavior of Al-Sn melts at 973 K. Thus, the present theoretical model is found to be suitable to explain the stability of Al-Sn melts at 973 K.

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